Surface melting of a macroscopic non-equilibrium system

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Agitated wet granular matter can be considered as a non-equilibrium model system for phase transitions, where the macroscopic particles replace the molecules and the capillary bridges replace molecular bonds. It is demonstrated experimentally that a two dimensional wet granular crystal driven far from thermal equilibrium melts from its free surface, preceded by an amorphous surface reshaping state. Both positional and orientational order parameters reveal that the transition into the surface melting state is a first order phase transition, with a transition threshold being traced to the rupture energy of single capillary bridges. This first time experimental observation of that transition in a macroscopic non-equilibrium system demonstrates the universality of surface melting.

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Surface melting has been a topic of interest since Michael Faraday's observations on regelation, the welding of two blocks of ice after contact below $0\,°C$ [1]. After more than a century's investigations, it becomes clear that melting is a continuous process that tends to start from the free surface [2–4]. The qualitative idea initiated by Frenkel [5] is the reduction of surface energy due to the weaker binding of molecules at the surface compared with that within the bulk. Quantitatively, a series of experiments pioneered by Frenken and colleagues [6, 7] have revealed that virtually all solids melt by forming a premelted film, an intermediate state between a solid and a liquid, below the bulk melting temperature [4]. Microscopic models have also been developed to describe surface melting [8]. However, how well can our current microscopic view of surface melting be applied to systems far from thermal equilibrium, and how far can the size of a crystal be scaled down for the surface melting behavior to persist, are questions of practical interest still lacking answers.

In this Letter, we demonstrate the universality of surface melting with a wet granular model system that is driven far from thermal equilibrium, as an extension of former investigations on the melting of colloidal and dry granular systems [9–14]. It is found that the melting of a two dimensional wet granular crystal under horizontal swirling motion is a two stage process: A deformation into a circular shape, followed by melting from the surface. The abrupt transition into the surface melting regime is reminiscent of a first order phase transition. The transition threshold can be traced down to the dissipation arising from the rupture of single capillary bridges.

The wet granular sample is prepared by adding a certain volume of purified water V_l into a monolayer of $N = 250$ cleaned black glass spheres (SiliBeads P), which has a density $\rho_p = 2.58$ g/cm^3 and a diameter $d = 4 \pm 0.02$ mm. The liquid content is defined as $W = V_l/V_s$ with V_s the total volume of the spheres.

The cylindrical container made of polytetrafluoroethylene (PTFE) has an inner diameter of 102 mm, a height of 6 mm, and a transparent glass lid to avoid evaporation of the liquid. It is fixed on a swirling table leveled within $5.7 \cdot 10^{-3}$ degrees to minimize the influence from gravity. The swirling table (see [15] for a sketch) provides a horizontal circular motion (i.e. a superposition of two horizontal vibrations in perpendicular directions) with a swirling frequency f and an amplitude $a = 31.8\pm0.1$ mm. The dynamics of the spheres are captured by a camera (Lumenera LU125M) mounted on the co-moving frame of the swirling table. The swirling frequency is obtained via tracing a fixed point on the swirling table with a second camera (Lumenera LU075M). The snapshots captured are subjected to an image processing procedure to locate all spheres based on a Hough transformation [16].

From the positions found, the connectivity of two neighboring particles is determined through a comparison
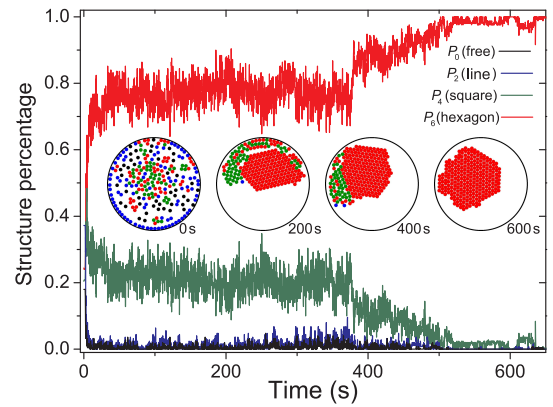

FIG. 1. Initialization process of a wet granular crystal, represented by the time evolution of the percentage for a particle to be free (P_0), or in a hexagonal (P_6), square (P_4), line (P_2) structure with swirling frequency $f = 1.693$ Hz and liquid content $W = 9.5\%$. Insets are sample images with particles color coded according to their local structures: Free particles with black; Line, square, hexagonal structures with blue, olive and red correspondingly.
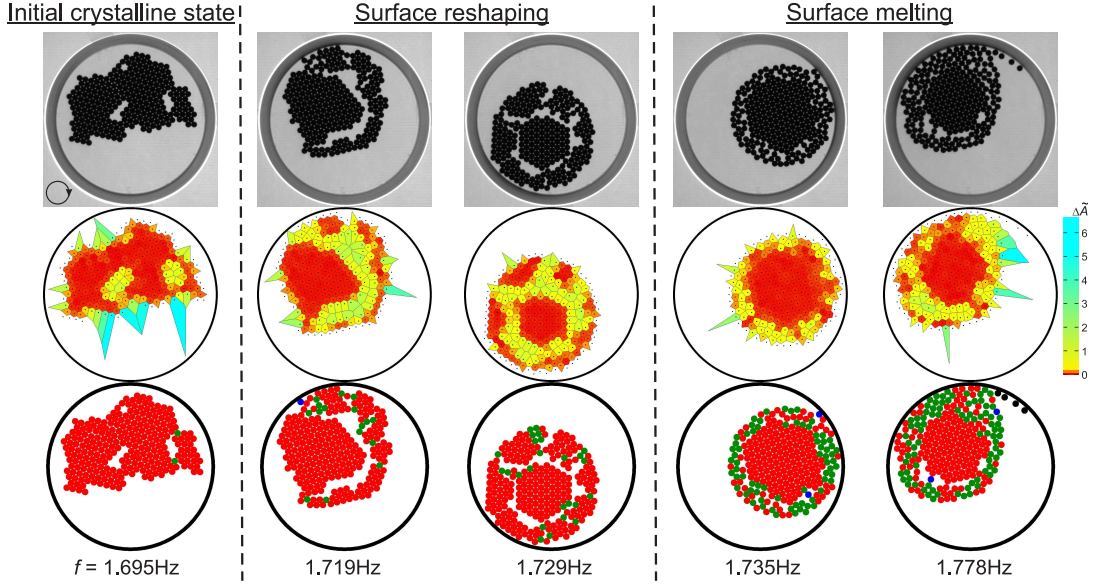
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FIG. 2. Melting process of an initially crystalline structure with increasing swirling frequency, represented by the snapshots (upper panel), Voronoi diagrams (middle panel), and local structures (lower panel). In the middle panel, only Voronoi cells inside the container are shown. They are color coded by $\Delta \tilde{A} = |A/A_{\mathrm{hex}} - 1|$, the deviation of the cell area A from that of a hexagonal structure $A_{\mathrm{hex}} = \sqrt{3}d^2/2$. The particles in the lower panel are color coded the same way as in the insets of Fig.1. Other parameters: particle number $N = 250$, liquid content $W = 8.4\%$, and swirling in the clockwise direction.

of their distance to the critical bond length $r_{\mathrm{b}} = 1.25\,d$, which is estimated from the rupture distance of a capillary bridge [17]. Local symmetries of particle configurations are characterized with the bond orientational order parameters (BOOP) [18, 19]. It is defined as $q_{\mathrm{l}} = \sqrt{\frac{4\pi}{2l+1}\sum_{m=-l}^{l}|\bar{Q}_{\mathrm{lm}}|^2}$, where $\bar{Q}_{\mathrm{lm}} \equiv \langle Q_{\mathrm{lm}}(\vec{r})\rangle$ is an average of the local order parameter $Q_{\mathrm{lm}}(\vec{r}) \equiv Y_{\mathrm{lm}}(\theta(\vec{r}), \phi(\vec{r}))$ over all bonds connecting one particle to its nearest neighbors, with $Y_{\mathrm{lm}}(\theta(\vec{r}), \phi(\vec{r}))$ spherical harmonics of a bond located at $\vec{r}$. Here, we choose q_6 as the order parameter because of its sensitivity to the hexagonal order. Based on the deviations of q_6 to the standard values for perfectly hexagonal, square and line structures, the structure that a particle is most likely belonging to is distinguished.

Figure 1 shows how the wet spheres organize into a crystalline state. In a rather short time scale (few seconds), initially isolated particles merge with each other into small assemblies. The amount of particles being free or in a line structure drops dramatically to 0, indicating a strong tendency of clustering. This tendency arises from the formation of capillary bridges between adjacent particles, which introduces a short ranged attractive potential. As a consequence, the amount of particles falling into a hexagonal structure (P_6) grows substantially to more than 60%. After this short time scale, most particles are condensed in a cluster that deforms continuously under swirling. As time evolves, more particles change from a square into a hexagonal structure. At about 500 seconds, a crystalline state with all particles in a hexagonal structure is reached. We consider this state to be stable,

since further colliding with the container does not lead to structure changes. Thus the initial crystalline state for the following experiments can be created via swirling at a moderate frequency for a period of 20 minutes.

Figure 2 shows the melting process as the swirling frequency grows. At $f = 1.695$ Hz, the particles form a crystalline structure with an irregular shape and defects inside. Although the crystal moves around collectively in the co-moving frame, the internal hexagonal structure keeps stable. As the frequency increases, the crystal starts to deform due to the breaking of capillary bridges mainly at the defects where the bonds are weaker. The broken bonds lead to larger voids within the cluster, along with more flexibility for various sub-components of the crystal to interact with each other, as the Voronoi diagrams indicate. As a consequence, the crystal changes into a more amorphous state with higher susceptibility to external disturbances. Visual inspections on the cluster indicate that it composes of a core with a perfect hexagonal packing (see the 1.729 Hz snapshot) shielded by several loosely connected small sub-components. Due to its interactions with the container, the cluster deforms continuous. However, melting has not yet started, since the BOOP results reveal that most particles, including those at the boundaries, still keep a local hexagonal structure.

Surface melting starts abruptly at a frequency between 1.729 Hz and 1.735 Hz, as the sudden change of the structure indicates. All the voids inside the cluster disappear suddenly and a state with a perfectly hexagonal core surrounded by few liquidlike layers arises. We identify the new state as surface melting, since local structures of the particles in the outer layers deviate from the hexagonal
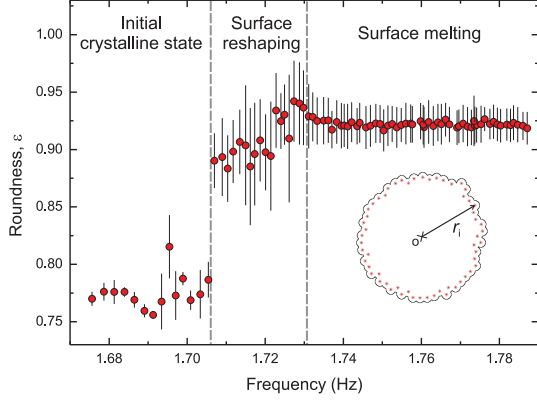
FIG. 3. Roundness ϵ of a wet granular cluster (see text for a definition) as a function of the swirling frequency. Inset: a processed image with edge particles (stars) determined from the distance to the cluster contour line. r_i is the distance between an edge particle and the cluster center O. The error represents the fluctuation of ϵ over continuous 300 frames. The gray dash lines correspond to 1.706 Hz and 1.731 Hz.

packing. Moreover, the melted layer tends to "wet" the crystalline core and keeps a circular shape, suggesting a tendency to reduce its surface energy.

To have a quantitative characterization of the melting process, we first analyze the roundness ϵ of the largest wet granular cluster as the swirling frequency grows. The roundness ϵ is defined as $1 - \sigma/r_{\max}$, where σ and $r_{\max}$ correspond to the standard deviation and maximum value of r_i. Here r_i is the distance of a particle at the edge to the center of mass of the cluster O (see the inset of Fig. 3). Note that $\epsilon = 1$ corresponds to a perfectly round surface. The clusters are distinguished by the connectivity of particles: Based on the criteria described above, we locate all the neighbors of a particle, and recursively the neighbors of all the neighbors found, until all particles inside a cluster are found.

As shown in Fig. 3, the abrupt growth of ϵ at $f \approx 1.706$ Hz suggests a transition from the crystalline state to surface reshaping. The threshold frequency is determined from the largest slope of the growth. As f increases, ϵ grows further until 0.93. Considering the roughness arising from the size of the particles, the saturated value ϵ suggests a circular shape. During the reshaping process, the cluster collides with the container wall more often than in the initial crystalline state. In the normal direction of the impact point, those collisions will generate wave propagation inside the cluster and effectively "heat" the particles. Different from the case of dry particles [20], the mechanical waves are more likely to be damped at the defects inside the cluster, reminiscent of the damping of seismic wave inside fault zones [21]. The enhanced energy dissipation effectively increases the susceptibility for the cluster to deform under the normal stress applied by the container. Meanwhile, the shear stress drives the rotation of the deforming cluster along the swirling direction.
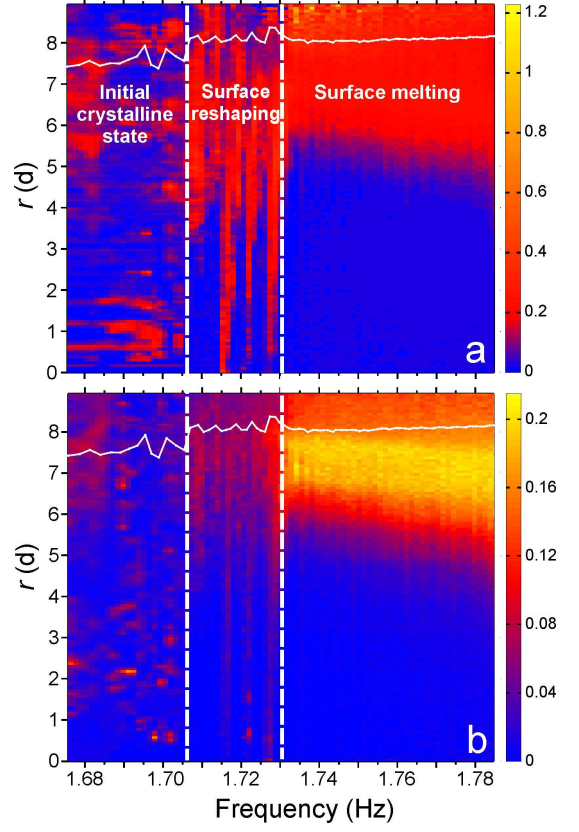

FIG. 4. Rescaled deviation of Voronoi cell area $\Delta \tilde{A}$ (a) and local BOOP $\Delta \tilde{q}_6$ (b) from a hexagonal close packing at various radial distance r (in unit of particle diameter d) to the cluster center, as a function of the swirling frequency. The white curve in either plot corresponds to a measure of the cluster size $(\bar{r}_i)$, which is averaged over all edge particles and over all frames recorded. The white dash lines (corresponding to the gray ones in Fig. 3) are guide to the eyes.

In the surface melting regime, the melted layer covering the crystalline core tends to keep a circular shape, since the roundness stays constantly at about 0.92. This is a manifestation of surface tension for fluidized wet granular matter [22]. Although the interactions with the container wall lead to temporary deformation of the cluster, the tendency of keeping a circular shape is robust for a wide frequency range. The slight decrease of ϵ above 1.78 Hz arises from the deformation of the melted layer due to the shear stress applied to the cluster.

Besides the surface deformation, the internal structure of the melting crystal is also characterized with a dimensionless Voronoi cell area $\Delta \tilde{A}$ (see caption of Fig. 2 for a definition), and $\Delta \tilde{q}_6 = |q_6/q_6^{\mathrm{hex}} - 1|$, where $q_6^{\mathrm{hex}} = 0.741$ is the two dimensional BOOP for a hexagonal close packing. To facilitate comparisons, we average both order parameters over all azimuth directions in a polar coordination system centered at O, and over all frames captured at a certain f.

As shown in Fig. 4, the two melting stages are clearly distinguishable from both order parameters. In the crys-
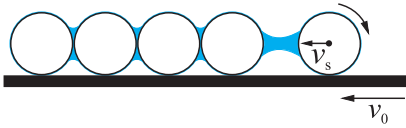
FIG. 5. A sketch illustrating a surface particle rolling away from the bulk. v_0 and v_s are the horizontal velocity of container, and that of the surface particle in the lab frame.

talline state, the hexagonal structure is widely kept inside the cluster, despite of small defects mostly originated from the initialization process. Those defects may persist as the frequency grows, suggesting that the energy injection is not sufficient to re-organize the cluster. As revealed by the orientational order parameter $\Delta \tilde{q}_6$ (b), the particles inside the crystal exhibit a strong tendency to keep a local hexagonal structure. In the surface reshaping regime, even though the positional order parameter (a) has a strong deviation from a crystalline structure, especially at outer layers, the small $\Delta \tilde{q}_6$ (b) suggests that the local bond orientational order is still kept. The growth of the mean cluster size in this regime can be attributed to the dilation of the cluster under reshaping. As the frequency increases further, both order parameters indicate an abrupt change into the surface melting regime at $f_{th} \approx 1.731$ Hz. Above this frequency, a more compact inner core with a size of about $6d$, covered with a melted layer of about $2d$, arises. Obvious deviations from a hexagonal close packing could be observed within the melted layer. The thickness of the melted layer is found to grow monotonically with the driving frequency, along with the growth of the cluster size.

In order to understand the melting threshold f_{th}, we propose a model based on a balance between the energy injection E_i and the total rupture energy of capillary bridges to mobilize a surface particle $E_i = n \cdot E_b$, with n the number of bridges to break and E_b the rupture energy for a single liquid bridge. The latter is estimated [23] to be $E_b = 4\pi\sigma\sqrt{V_b d/2}$, with $\sigma = 0.072$ N/m surface tension of water and the bridge volume $V_b = \pi d^3 W/(3N_{cor})$. Assuming a cluster of 250 particles in a hexagonal close structure, the coordination number $N_{cor} \approx 5.5$.

The collective motion of the cluster is driven by its interactions with the container under horizontally swirling motion. Since the motion is a superposition of two sinusoidal vibrations perpendicular to each other, we consider a one dimensional case for the sake of simplicity. As sketched in Fig. 5, the surface particle has more freedom to roll compared with those in the bulk, due to less restrictions from its neighbors. Assuming the extreme case that only surface particles can roll, and roll without sliding and rolling frictions, we estimate the translational velocity of the surface particle to be $v_s = 2v_0/7$ [24], where $v_0 = 2\pi f a$ is the velocity of the orbit motion. Therefore, the energy injection (i.e. the kinetic energy gained by the surface sphere in the co-moving frame) is $E_i = \frac{50}{49}m(\pi f a)^2$ with m the mass of the sphere. Consequently, we can estimate the threshold frequency $f_{th} = \frac{1.313}{a}(\frac{\sigma n}{\rho_p d})^{\frac{1}{2}}(\frac{W}{N_{cor}})^{\frac{1}{4}} \approx 1.72$ Hz with $n = 2$, and other known parameters. The critical number of broken bridges $n = 2$ is plausible, since particles at edges of a cluster with initially 3 neighbors are the easiest to become mobile via breaking two bridges.

In summary, the melting of a two dimensional wet granular crystal with 250 macroscopic "molecules" is demonstrated to be a continuous process starting from the surface. Preceding to the start of melting, there exists an intermediate stage where the crystal deforms into a circular shape, leading to a more fragile internal structure with large fluctuations of voids. The abrupt transition into the surface melting regime, reminiscent of a first order phase transition, can be rationalized with the balance of the energy injection and dissipation through the rupture of capillary bridges. The behavior of surface melting for wet granular crystal suggests a complete wetting of the melted layer and a tendency to minimize the surface energy [3, 25], although the analogue of an interfacial tension in our macroscopic non-equilibrium system has not yet been worked out.

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